09Fall 化工熱力學

Ch.4

Entropy and Its Balance Equation

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Outline

1. What Is Entropy?
2. Entropy Balance and Reversibility
3. Engines and Entropy
4. Entropy Changes of Matter

What is entropy?

- Mass and energy balance equations are not always sufficient to solve all the thermodynamic energy flow problems
- Need a balance equation for an additional state variable -- entropy.
- Unidirectional character of natural processes (All spontaneously processes proceed only in the direction that tends to dissipate the gradients in the system => lead to equilibrium state and never in the reverse direction <= entropy.

For any extensive variable θ of a closed, isolated, constant volume system

$$\frac{d\theta}{dt} = \left(\text{rate at which } \theta \text{ enters the system}\right) - \left(\text{rate at which } \theta \text{ leaves the system}\right) + \dot{\theta}_{gen}$$

Goals

- Use entropy balance for problem solving
- Calculate the entropy change between two states of an ideal gas
- Calculate the entropy change of a real fluid using thermodynamic properties charts and tables

Entropy

- At equilibrium, $\frac{d\theta}{dt} = 0 \Rightarrow \dot{\theta}_{gen} = 0 \text{ and } \theta = constant$
- Let $\dot{\theta}_{gen} > 0 \Rightarrow \frac{d\theta}{dt} > 0,\ away\ from\ equilibrium$
- θ is monotonically increasing and reaches to a maximum at equilibrium state.
- θ represents the unidirectional evolution of a system to the equilibrium state.
- Find a variable θ that

$$\dot{\theta}_{gen} \geq 0$$

The variable θ is a nonconserved variable and a state variable.

- Definition of entropy, *S*: Let entropy (*S*) is a state function. The rate of entropy change results from the heat flow is *Q*/*T*, where *T* is the absolute thermodynamic temperature of the system at the point of the heat flow. If there are mass flows across the boundaries, the total entropy of the system will also change due to this convected flow.

Equilibrium and Spontaneity

- For an isolated constant-volume system, spontaneous process occurs and leads the system to a state of equilibrium.
  - For the balance of any property θ, $\frac{d\theta}{dt} = \dot{\theta}_{gen}$
  - At equilibrium (the final state), $\frac{d\theta}{dt} = \dot{\theta}_{gen} = 0$
  - Thus, we conclude that

    at equilibrium, θ = constant or $\frac{d\theta}{dt} = 0$

    away from equilibrium, $\frac{d\theta}{dt} \neq 0 \ (> 0 \text{ or } < 0)$
  - If $\frac{d\theta}{dt} > 0$ then θ is increased during this process.

    If $\frac{d\theta}{dt} < 0$ then θ is decreased during this process.
  - Following the changes of a suitable θ can tell the direction of the spontaneous process.

Entropy: A New Concept

- Definition of Entropy

The entropy (S) is a state function. In a system in which there are flows of both heat and work across the boundaries, the heat flow, but not the work flow, causes a change in the entropy of the system; this rate of entropy change is $\dot{Q}/T$, where T is the absolute thermodynamic temperature of the system at the point of the heat flow. If, in addition, there are mass flows across the system boundaries, the total entropy of the system will also change due to this convection flow. That is, each element of mass entering or leaving the system carried with it its entropy.

$$\frac{dS}{dt}=\frac{\dot{Q}}{T} \quad \text{or} \quad dS=\frac{dQ}{T} \quad \text{or} \quad \Delta S=\int \frac{dQ}{T}$$

Q is a path property !!??

Entropy Balance Equation

$$\frac{dS}{dt}=\sum \dot{M}_k\hat{S}_k+\frac{\dot{Q}}{T}+\dot{S}_{gen} \quad (4.1\text{-}5a)$$

- **For a closed system**

$$\frac{dS}{dt}=\frac{\dot{Q}}{T}+\dot{S}_{gen} \quad (4.1\text{-}5b)$$

- **For a closed system and through a reversible process**

$$\boxed{\frac{dS}{dt}=\frac{\dot{Q}^{rev}}{T}}$$

Reversible & Adiabatic => Isentropic

- **The second law of thermodynamics**

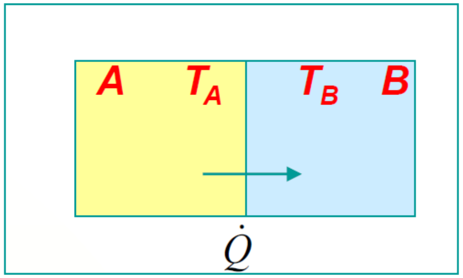
$$\dot{S}_{gen}\geq 0,\ \ and\ \ \frac{dS}{dt}=0\ at\ equilibrium \quad (4.1\text{-}5c)$$

- **Show that**
  - **(1) S is a state function**

    $(2)\ \dot{S}_{gen}\geq 0$

Since entropy generation depends on the detailed internal relaxation processes, we consider the following thermodynamic system.

Thermal Contact



- *To evaluate the entropy change of subsystems, we construct a successive equilibrium heat transfer process.*
- *The subsystems A and B are passing through a succession of equilibrium states (i.e., quasistatic process)*

$$\dot{S}_{gen} = 0 \Rightarrow \frac{dS_i}{dt} = \frac{Q_i^{rev}}{T_i}$$

- For subsystem A

$$\frac{dS_A}{dt} = \frac{Q_A^{rev}}{T_A} = \frac{-h(T_A - T_B)}{T_A}$$

- For subsystem B

$$\frac{dS_B}{dt} = \frac{Q_B^{rev}}{T_B} = \frac{-h(T_B - T_A)}{T_B}$$

$$\dot{Q}_A^{rev} = -\dot{Q}_B^{rev} = -h(T_A - T_B)$$

- The entropy balance for the isolated, nonequilibrium composite system:

$$\frac{dS}{dt} = \dot{S}_{gen} = \frac{d(S_A + S_B)}{dt} = \frac{h(T_A - T_B)^2}{T_A T_B} \geq 0$$

- Rate of entropy generation is positive
- Rate of entropy generation is proportional to the second power of the system nonuniformity.

$$\dot{S}_{gen} \propto (\Delta T)^2$$

General Entropy Balance Equations

- Differential form

$$\frac{dS}{dt} = \sum \dot{M}_k \hat{S}_k + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

- Difference form

$$S_2 - S_1 = \sum \int_{t1}^{t2} \dot{M}_k \hat{S}_k dt + \int_{t1}^{t2} \frac{\dot{Q}}{T} dt + S_{gen}$$

$$where\ S_{gen} = \int_{t1}^{t2} \dot{S}_{gen} dt \quad (total\ entropy\ generated)$$

Illustration 4.1-1 Clausius Statement of the Second Law

- It is not possible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a colder body to a hotter body.
- Show from the axiom $S_{gen} > 0$ that the process below is impossible.

For one complete cycle

Energy balance over one complete cycle:

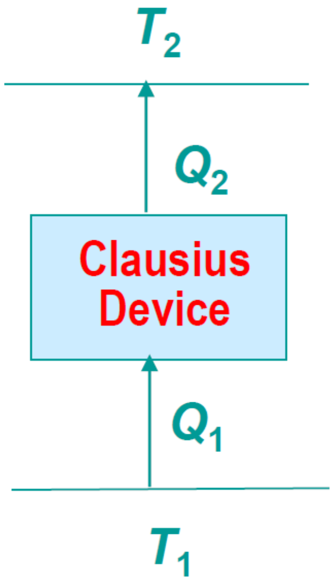
$$U_f - U_i = 0 = Q_1 + Q_2 + \cancel{W}$$

$$Q_2 = -Q_1 \ (possible)$$

Entropy balance over one complete cycle:

$$S_f - S_i = 0 = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + S_{gen}$$

$$\therefore \quad S_{gen} = -\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = \frac{Q_1}{T_2} - \frac{Q_1}{T_1} = Q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$



$T_2 > T_1$

- **Since $T_2 > T_1$, if Q_1 was positive (heat flow into device from cold body) then $S_{gen} < 0$ (impossible).**
- **If Q_1 was negative (heat flow from high T to low T) or Q_1 was positive and $T_1 > T_2$, $S_{gen} > 0$ (possible).**
- **The statement of the second law, $S_{gen} > 0$, is consistent with the Clausius version, but much more general than it.**

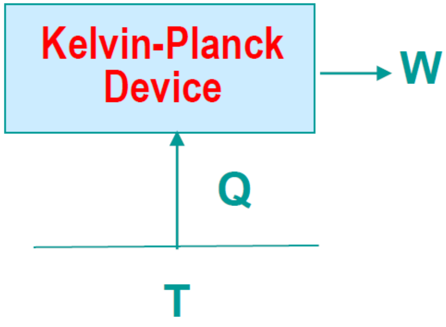
Illustration 4.1-2 Kelvin-Planck statement of 2nd law

<It is not possible to construct a device operating in a cycle that results in no effect other than the production of work by transferring heat from a single body>

<sol> Energy balance over one complete cycle:

$$U_f - U_i = 0 = Q + W$$

$$W = -Q \ (possible)$$



Entropy balance over one complete cycle:

$$S_f - S_i = 0 = \frac{Q}{T} + S_{gen}$$

$$S_{gen} = -\frac{Q}{T} < 0 \ (impossible)$$

- **Heat can not be completely converted to work in a cyclic process.**
- **If *W* is positive and *Q* is negative, the process is possible.**
- **Work can be completely converted to heat in a cyclic process. Heat is less useful than Work.**

The entropy balance and reversibility

- **Reversible processes => equilibrium =>** $\dot{S}_{gen} = 0$

$$\dot{S}_{gen} \propto (system\ gradient)^2,\ e.g.,\ (\nabla T)^2$$

$$rate\ of\ internal\ relaxation\ processes \propto (system\ gradient)^1,\ e.g.,\ (\nabla T)$$

$$If\ small\ (\nabla T) \rightarrow q \Rightarrow \dot{S}_{gen}\left[\propto (\nabla T)^2\right] \approx negligible$$

- **A process occurs with small gradients in temperature and velocity**
  => the rate of entropy generation is essentially zero
  => the process can be considered to be reversible
- **Observations:**
  - **Observe an open system during 0 => *t_1* and *t_1* => *t_2*, where *t_2* = 2*t_1*.**

$$Mass\ Bal.:\ M_2 - M_0 = \sum_k \int_0^{t_1} \dot{M}_k dt + \sum_k \int_{t_1}^{t_2} \dot{M}_k dt$$

$$Engergy\ Bal.:\ U_2 - U_0 = \int_0^{t_1} \left[\sum_k \dot{M}_k \hat{H}_k - P\frac{dV}{dt} + \dot{W}_s + \dot{Q} \right] dt + \int_{t_1}^{t_2} \left[\sum_k \dot{M}_k \hat{H}_k - P\frac{dV}{dt} + \dot{W}_s + \dot{Q} \right] dt$$

$$Entropy\ Bal. = S_2 - S_0 = \int_0^{t_1} \left[\sum_k \dot{M}_k \hat{S}_k + \frac{\dot{Q}}{T} \right] dt + \int_{t_1}^{t_2} \left[\sum_k \dot{M}_k \hat{S}_k + \frac{\dot{Q}}{T} \right] dt + \int_0^{t_1} \dot{S}_{gen} dt + \int_{t_1}^{t_2} \dot{S}_{gen} dt$$

Entropy: A New Concept

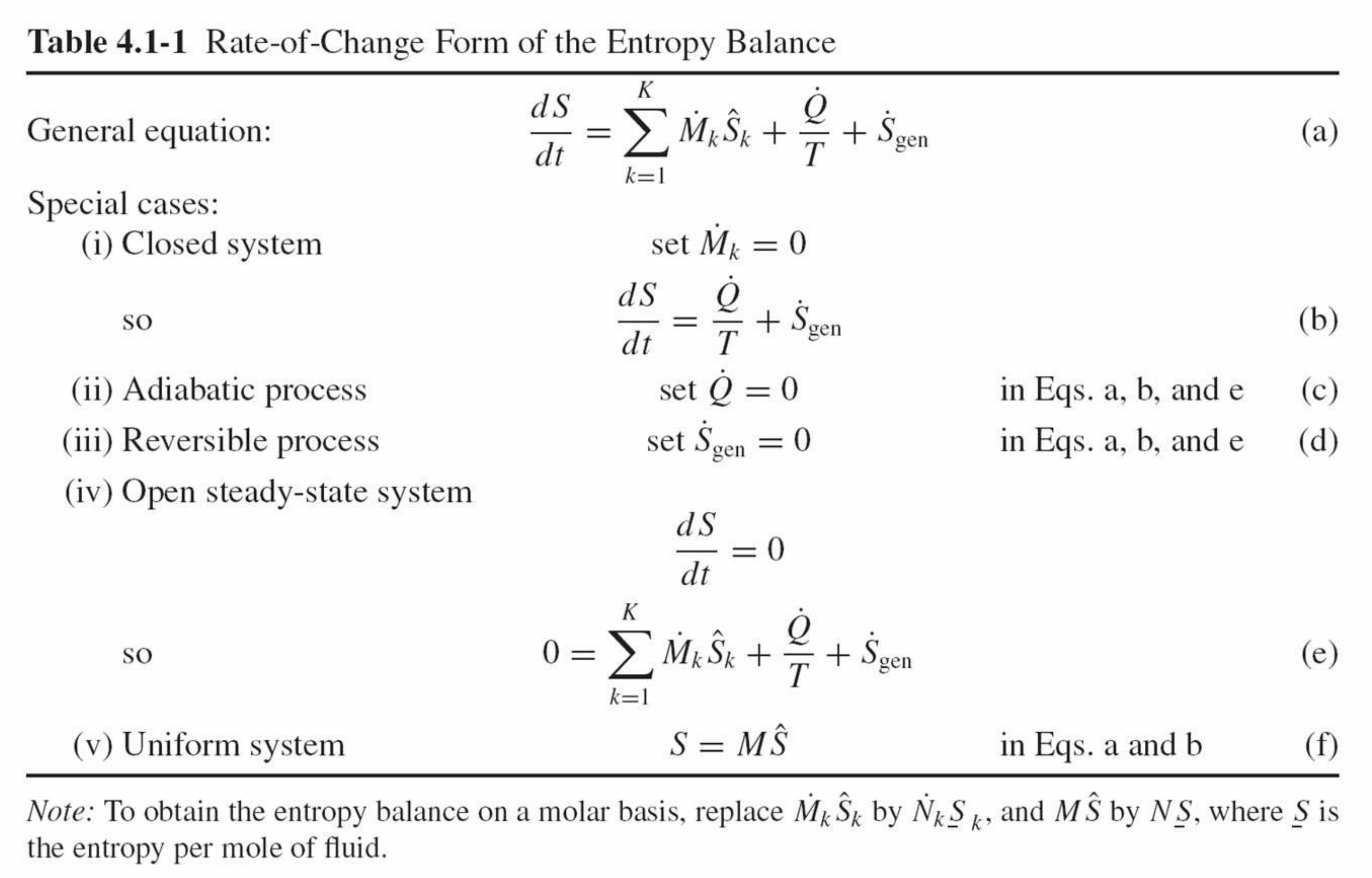


Table 4.1-1 Rate-of-Change Form of the Entropy Balance

General equation:	$\frac{dS}{dt} = \sum_{k=1}^{K} \dot{M}_k \hat{S}_k + \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}$		(a)
Special cases:			
(i) Closed system	set $\dot{M}_k = 0$		
so	$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}$		(b)
(ii) Adiabatic process	set $\dot{Q} = 0$	in Eqs. a, b, and e	(c)
(iii) Reversible process	set $\dot{S}_{\text{gen}} = 0$	in Eqs. a, b, and e	(d)
(iv) Open steady-state system	$\frac{dS}{dt} = 0$		
so	$0 = \sum_{k=1}^{K} \dot{M}_k \hat{S}_k + \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}$		(e)
(v) Uniform system	$S = M\hat{S}$	in Eqs. a and b	(f)

Note: To obtain the entropy balance on a molar basis, replace $\dot{M}_k \hat{S}_k$ by $\dot{N}_k \underline{S}_k$, and $M\hat{S}$ by $N\underline{S}$, where $\underline{S}$ is the entropy per mole of fluid.

Entropy: A New Concept

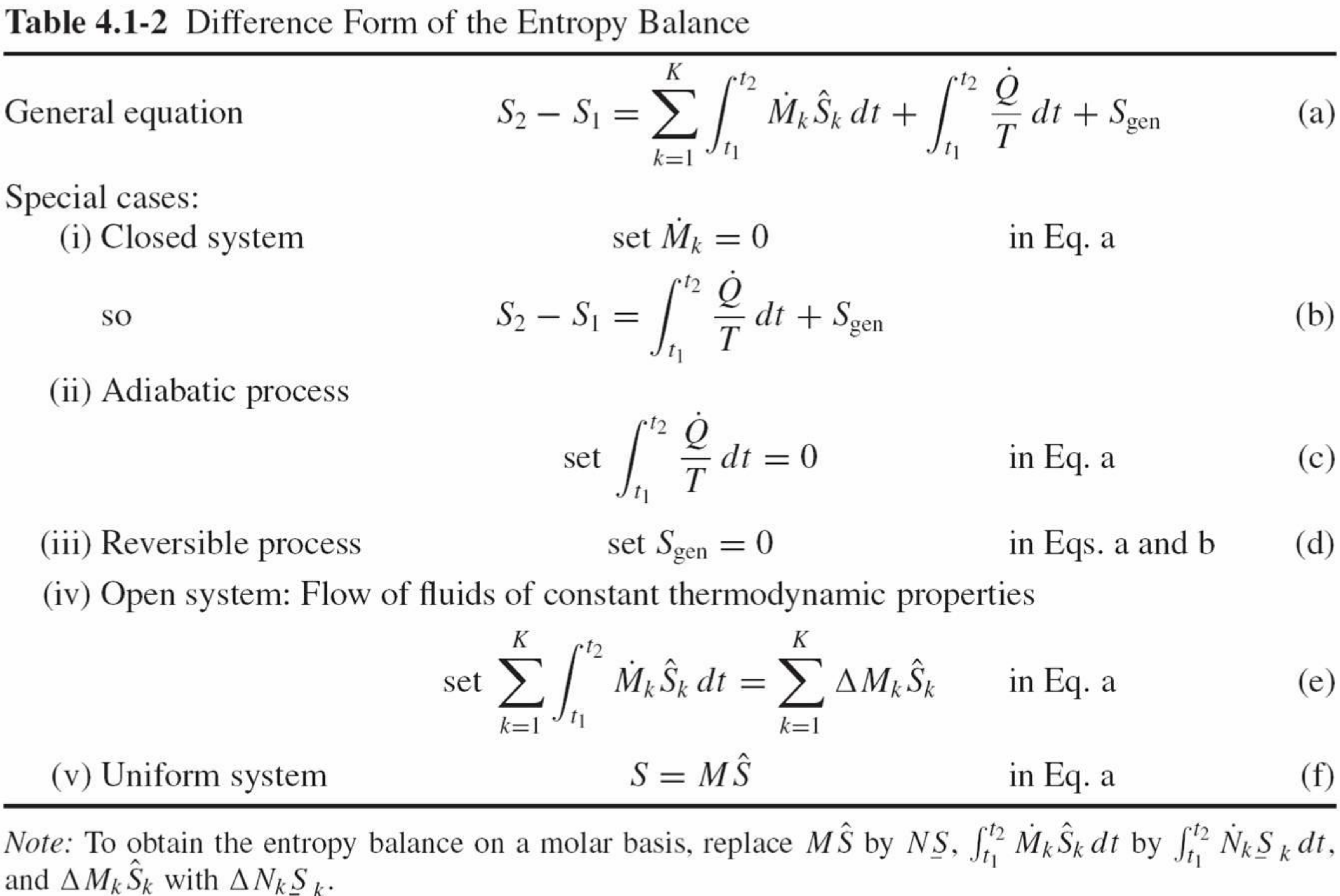


Table 4.1-2 Difference Form of the Entropy Balance

General equation	$S_2 - S_1 = \sum_{k=1}^{K} \int_{t_1}^{t_2} \dot{M}_k \hat{S}_k \, dt + \int_{t_1}^{t_2} \frac{\dot{Q}}{T} \, dt + S_{\text{gen}}$		(a)
Special cases:			
(i) Closed system	set $\dot{M}_k = 0$	in Eq. a	
so	$S_2 - S_1 = \int_{t_1}^{t_2} \frac{\dot{Q}}{T} \, dt + S_{\text{gen}}$		(b)
(ii) Adiabatic process			
	set $\int_{t_1}^{t_2} \frac{\dot{Q}}{T} \, dt = 0$	in Eq. a	(c)
(iii) Reversible process	set $S_{\text{gen}} = 0$	in Eqs. a and b	(d)
(iv) Open system: Flow of fluids of constant thermodynamic properties			
	set $\sum_{k=1}^{K} \int_{t_1}^{t_2} \dot{M}_k \hat{S}_k \, dt = \sum_{k=1}^{K} \Delta M_k \hat{S}_k$	in Eq. a	(e)
(v) Uniform system	$S = M\hat{S}$	in Eq. a	(f)

Note: To obtain the entropy balance on a molar basis, replace $M\hat{S}$ by $N\underline{S}$, $\int_{t_1}^{t_2} \dot{M}_k \hat{S}_k \, dt$ by $\int_{t_1}^{t_2} \dot{N}_k \underline{S}_k \, dt$, and $\Delta M_k \hat{S}_k$ with $\Delta N_k \underline{S}_k$.

Reversibility

- **If all the mass, heat, and work flows are reversed between t_1 and t_2 from that between 0 and t_1,**

$$Mass\ Bal.:\ M_2 - M_0 = 0 \Rightarrow\ M_2 = M_0$$

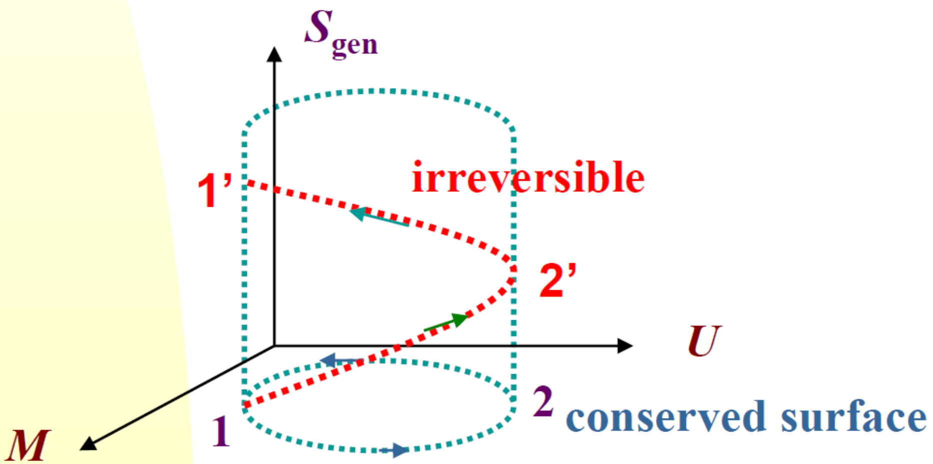
$$Engergy\ Bal.:\ U_2 - U_0 = 0 \Rightarrow\ U_2 = U_0$$

$$Entropy\ Bal. = S_2 - S_0 = \int_0^{t_1} \dot{S}_{gen} dt + \int_{t_1}^{t_2} \dot{S}_{gen} dt \Rightarrow\ S_2 = S_0 + \int_0^{t_1} \dot{S}_{gen} dt + \int_{t_1}^{t_2} \dot{S}_{gen} dt$$

$$S_2 \geq S_0\ (initial\ state\ and\ final\ state\ may\ be\ different) \Leftarrow\ irreversible$$

- If the change process is infinitesimal =>

$$\dot{S}_{gen} = 0\ and\ S_2 = S_0 \Leftarrow\ reversible$$



Examples of reversible and irreversible process

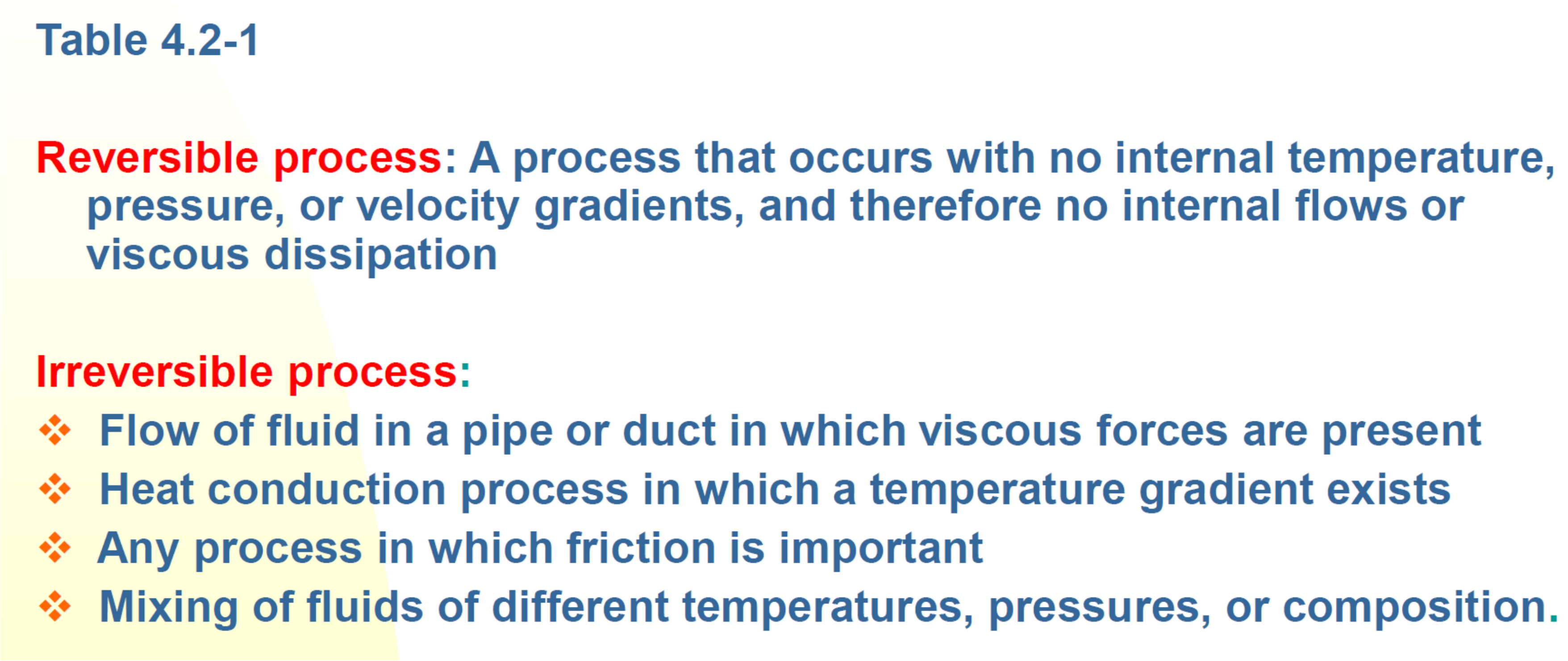


Table 4.2-1

Reversible process: A process that occurs with no internal temperature, pressure, or velocity gradients, and therefore no internal flows or viscous dissipation

Irreversible process:

- Flow of fluid in a pipe or duct in which viscous forces are present
- Heat conduction process in which a temperature gradient exists
- Any process in which friction is important
- Mixing of fluids of different temperatures, pressures, or composition.

The characteristics of reversible process

- **Reversible processes:**
  - **Maximum amount of work is obtained.**
  - **Minimum amount of work is needed.**
  - **An upper or lower limit for real systems**
- **For a closed, constant *T* and *V* system:**

$$energy\,balance: U_2 - U_1 = \sum_k \int_{t1}^{t2} \cancel{\dot{M}_k \hat{H}_k}\, dt + Q + W_s - \int P \cancel{\frac{dV}{dt}}\, dt \quad \Rightarrow U_2 = U_1 + Q + W_s \qquad (a)$$

$$entropy\,balance: S_2 - S_1 = \sum_k \int_{t1}^{t2} \cancel{\dot{M}_k \hat{S}_k}\, dt + \int_{t1}^{t2} \frac{\dot{Q}}{T} dt + S_{gen} \quad \Rightarrow S_2 = S_1 + \frac{Q}{T} + S_{gen} \qquad (b)$$

Let *T* = *T*$_1$ = *T*$_2$ and from eqs. (a) and (b), we get

$$W_s = \left(U_2 - T_2 S_2\right) - \left(U_1 - T_1 S_1\right) + TS_{gen} = A_2 - A_1 + TS_{gen}$$

$$where\ A = U - TS \quad < Helmholtz\ free\,energy >$$

$$W_s^{rev} = A_2 - A_1 \quad for\,closed\,and\,constant\,T\ \&\ V\ system$$

$$W_s = W_s^{rev} + TS_{gen} \Rightarrow$$

$$\because S_{gen} > 0 \Rightarrow W_s \geq W_s^{rev}$$

- ***W* > 0 (work required) *W*^{rev} is min.**
- ***W* < 0 (work done by the system) *W*^{rev} is max.**

The characteristics of reversible process

- **For a closed, constant *T* and *P* system:**

$$\text{energybalance:}\, U_2 - U_1 = \cancel{\sum_k \int_{t1}^{t2} \dot{M}_k \hat{H}_k dt} + Q + W_s - \int P\frac{dV}{dt}dt \quad \Rightarrow U_2 = U_1 + Q + W_s - (P_2V_2 - P_1V_1) \quad (c)$$

$$\text{entropybalance:}\, S_2 - S_1 = \cancel{\sum_k \int_{t1}^{t2} \dot{M}_k \hat{S}_k dt} + \int_{t1}^{t2}\frac{\dot{Q}}{T}dt + S_{gen} \quad \Rightarrow S_2 = S_1 + \frac{Q}{T} + S_{gen} \quad (d)$$

Let $T = T_1 = T_2$, $P = P_1 = P_2$ and from eqs. (c) and (d), we have

$$W_s = (U_2 + P_2V_2 - T_2S_2) - (U_1 + P_1V_1 - T_1S_1) + TS_{gen} = G_2 - G_1 + TS_{gen}$$

$$\text{where}\, G = U + PV - TS = H - TS \quad <\text{Gibbs free energy}>$$

$$W_s^{rev} = G_2 - G_1 \;\; \text{for closed and constant} \, T \,\&\, P \, \text{system}$$

$$\text{again,} W_s = W_s^{rev} + TS_{gen}$$

For a reversible process in a closed system

$$Q^{rev} = U_2 - U_1 - W^{rev}$$

$$\text{For a real process,} Q = U_2 - U_1 - W = U_2 - U_1 - W^{rev} - TS_{gen}$$

$$\Rightarrow Q = Q^{rev} - TS_{gen} \; (\text{less heat is required for an irreversible process})$$

$$\Rightarrow W = W^{rev} + TS_{gen} \; (\text{more work is required for an irreversible process})$$

$$\Rightarrow (-W^{rev}) - (-W) = TS_{gen} \; (\text{lost work})$$

- **e.g., (work required) 100 = 80 + 20 & (work done) -100 = -120 + 20**
- **Mechanical work => thermal energy (TS_{gen}) due to irreversibility**
  => effective work

Evaluate entropy changes from other state variables

- **Assumptions:**
  - *Open system*
  - *KE & PE terms are neglected*
  - *Only one mass flow stream*
  - *Mass and heat flows occur at the same T*

$$\text{Mass Bal.:}\quad \frac{dM}{dt} = \dot{M}$$

$$\text{Energy Bal.:}\quad \frac{dU}{dt} = \dot{M}\,\hat{H} + \dot{Q} - P\frac{dV}{dt} + \dot{W}_s$$

$$\text{Entropy Bal.:}\quad \frac{dS}{dt} = \dot{M}\,\hat{S} + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\Rightarrow\quad \frac{dU}{dt} = \hat{H}\frac{dM}{dt} + \dot{Q} - P\frac{dV}{dt} + \dot{W}_s$$

$$T\frac{dS}{dt} = T\,\hat{S}\frac{dM}{dt} + \dot{Q} + T\,\dot{S}_{gen}$$

$$dU = \hat{H}\,dM + Q - PdV + W_s$$

$$TdS = T\,\hat{S}\,dM + Q + TS_{gen}$$

$$\Rightarrow\quad dU = TdS - TS_{gen} - PdV + W_s + \hat{G}\,dM$$

- **For a reversible process (S_{gen} = 0)**

$$Q^{rev} = T\,dS - T\,\hat{S}\,dM \text{ (only valid for reversible processes)}$$

$$dU = T\,dS + \left(-PdV + W_s\right)^{rev} + \hat{G}\,dM$$

$$Q^{rev} = Q^{irrev} + TS_{gen}$$

$$\left(-PdV + W_s\right)^{rev} = \left(-PdV + W_s\right)^{irrev} - TS_{gen}$$

- **For a system without shaft work**
- **For a closed system without shaft work**

$$\Rightarrow\quad dU = TdS - PdV + \hat{G}\,dM$$

$$dU = TdS - PdV$$

Fundamental thermodynamic relationship

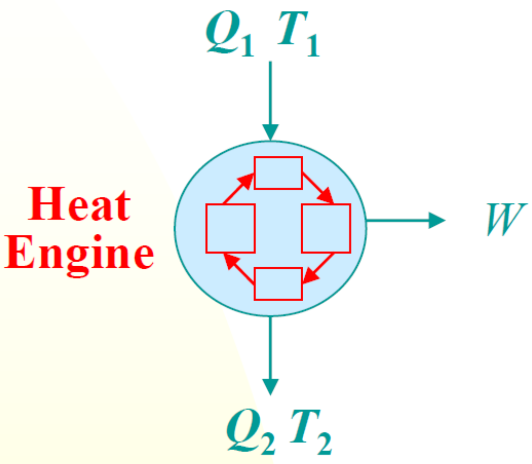
$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V$

- Only state variables in the above equation
- The equation is valid, regardless of the paths and the systems
- It is a fundamental thermodynamic relation

- Energy functions
  - $U \quad \Rightarrow \quad \mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V \quad \Rightarrow \quad U = f\,(S, V)$
  - $H = U + PV \quad \Rightarrow \quad \mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P \quad \Rightarrow \quad H = f\,(S, P)$
  - $A = U - TS \quad \Rightarrow \quad \mathrm{d}A = -P\,\mathrm{d}V - S\,\mathrm{d}T \quad \Rightarrow \quad A = f\,(T, V)$
  - $G = H - TS \quad \Rightarrow \quad \mathrm{d}G = V\,\mathrm{d}P - S\,\mathrm{d}T \quad \Rightarrow \quad G = f\,(T, P)$

Heat, work, and entropy

Heat => heat engine => work



For a steady-state operation or a cyclic system:

$$\text{Energy balance} \quad 0 = Q_1 + Q_2 + W \qquad (1)$$

$$\text{Entropy balance} \quad 0 = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + S_{gen} \qquad (2)$$

$$\Rightarrow \text{Work done by the engine} = -W = Q_1\left(\frac{T_1 - T_2}{T_1}\right) - T_2\, S_{gen} \qquad (3)$$

- **Maximum work is obtained if S_{gen} = 0 (reversible):**

$$(-W)_{max} = Q_1\left(\frac{T_1 - T_2}{T_1}\right)$$

$$(\text{engine efficiency } \eta)_{max} = \frac{(-W)_{max}}{Q_1} = \frac{T_1 - T_2}{T_1} = f(T_1, T_2)\ \text{only}$$

$$\text{e.g.,} T_1 = 300^o\,C = 573\,K, T_2 = 40^o\,C = 313\,K \Rightarrow \eta_{max} = \frac{573 - 313}{573} = 0.40$$

$$\eta_{actual} \approx 0.5\,\eta_{max}$$

Heat, work, and entropy

From eqs. (1) and (3):

$$\boxed{\begin{array}{l} -Q_2 = Q_1 \dfrac{T_2}{T_1} + T_2 S_{gen} \\ (>0) \quad (>0) \qquad (>0) \end{array}}$$

- It is impossible to convert all the heat supplied to engine into work ($Q_2 = 0$), unless $T_2 = 0$ K and reversible.
- Work (> 0) can completely convert into heat.

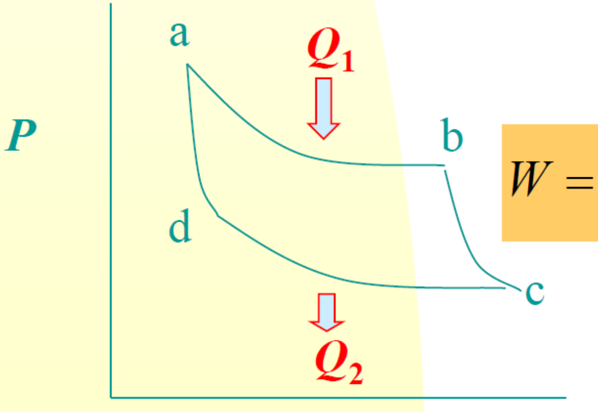
  energy balance: $-Q_2 = Q_1 + W$

  Eq. (3): $S_{gen} = Q_1 [(1/T_2) - (1/T_1)] + (W/T_2)$

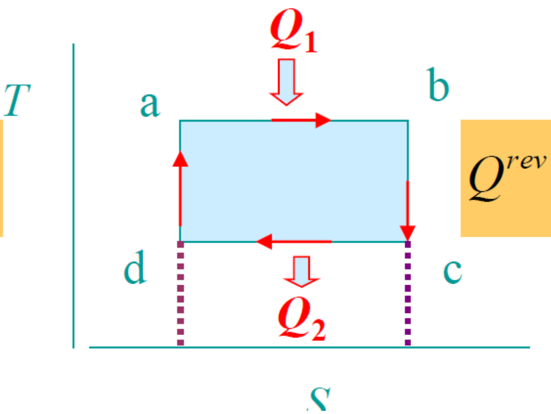
  $(>0) \quad (>0) \qquad (>0) \qquad\qquad (>0)$
- Mechanical energy can be considered as a higher quality of energy than thermal energy.

Engine to give maximum efficiency(Carnot engine)

		process	work	heat
1	a => b	reversible & isothermal expansion	$-\int_{V_a}^{V_b} PdV\ (<0)$	$Q_1\ (>0)$
2	b => c	reversible & adiabatic expansion	$-\int_{V_b}^{V_c} PdV\ (<0)$	0
3	c => d	reversible & isothermal compression	$-\int_{V_c}^{V_d} PdV\ (>0)$	$Q_2\ (<0)$
4	d => a	reversible & adiabatic compression	$-\int_{V_d}^{V_a} PdV\ (>0)$	0



$$W = -\int_{V_i}^{V_f} P\,dV$$



$$Q^{rev} = \int_{S_i}^{S_f} T\,dS$$

Carnot engine

- **For one complete cycle:**

$$0 = W + Q_1 + Q_2$$

$$0 = \frac{Q_1}{T_1} + \frac{Q_2}{T_2}$$

$$\text{where}\, W = -\int_{V_a}^{V_b} P\,dV - \int_{V_b}^{V_c} P\,dV - \int_{V_c}^{V_d} P\,dV - \int_{V_d}^{V_a} P\,dV$$

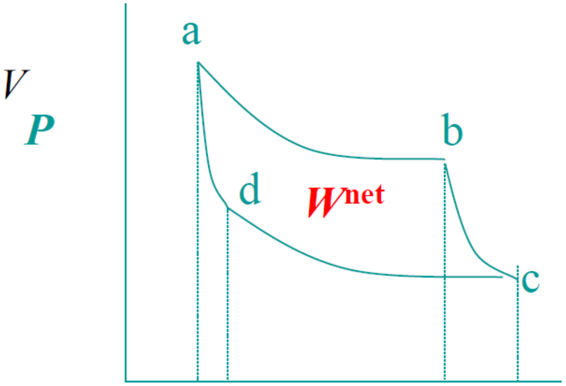
$$\therefore \quad -W^{Carnot} = Q_1 - \left(\frac{T_2}{T_1} Q_1 \right) = \left(\frac{T_1 - T_2}{T_1} \right) Q_1$$

$$\eta^{Carnot} = \frac{-W}{Q_1} = \frac{T_1 - T_2}{T_1} = \eta^{max}$$

- **Carnot engine is the most efficient engine.**
- **Its efficiency is independent of the working fluid.**

Work from PV diagram and Q from TS diagram

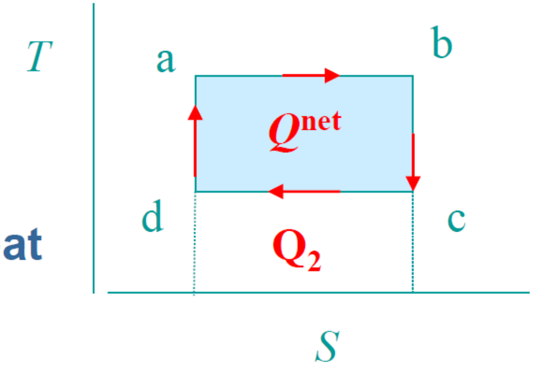
- **Work supplied by Carnot engine,** $W = -\int P\,dV$
- $-W^{net} = -(W_{ab} + W_{bc} + W_{cd} + W_{da})$
  $= \text{area (a-b-c-d) in } PV \text{ diagram}$
  $= \text{work done by the Carnot engine}$



- Differential entropy change corresponds with the differential heat flow d*Q* for a reversible process in a closed system:

$$dS = \frac{\delta Q^{rev}}{T} \Rightarrow Q^{rev} = \int T\,dS$$

  - It is valid for irreversible processes with heat transfer only. $\Delta U = Q + \cancel{W} = Q^{rev} = Q^{irrev}$



$$Q^{net} = |Q_1| - |Q_2| = -W^{net}$$
$$= area\,(a-b-c-d)\ in\ TS\ diagram$$

Fluid flow engine (Turbine)

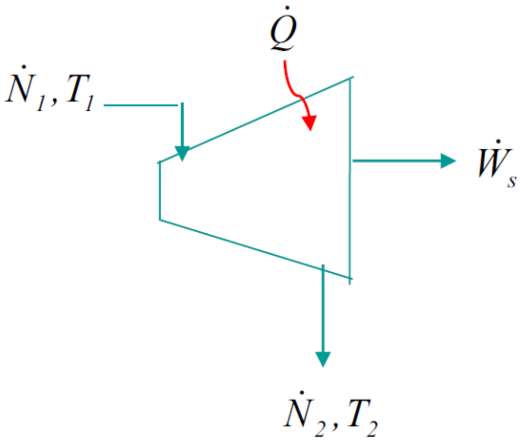
- **Convert the thermal energy of a flowing flow into mechanical work.**
- **At steady state,**

$$\boxed{\begin{aligned}
&0=\dot{N}_1+\dot{N}_2 \quad\Rightarrow\quad \dot{N}_1=-\dot{N}_2\\
&0=\left(\underline{H}_1-\underline{H}_2\right)\dot{N}_1+\dot{Q}+\dot{W}_s\\
&0=\left(\underline{S}_1-\underline{S}_2\right)\dot{N}_1+\frac{\dot{Q}}{T}+\dot{S}_{gen}
\end{aligned}}$$

$$\dot{Q}=-T\left(\underline{S}_1-\underline{S}_2\right)\dot{N}_1-T\dot{S}_{gen}$$

$$\dot{W}_s=-\dot{N}_1\left[\left(\underline{H}_1-T\underline{S}_1\right)-\left(\underline{H}_2-T\underline{S}_2\right)\right]+T\dot{S}_{gen}$$

$$\text{note : } \underline{H}_1-T\underline{S}_1\neq\underline{H}_1-T_1\underline{S}_1=\underline{G}_1,\ \text{unless } T=T_1$$



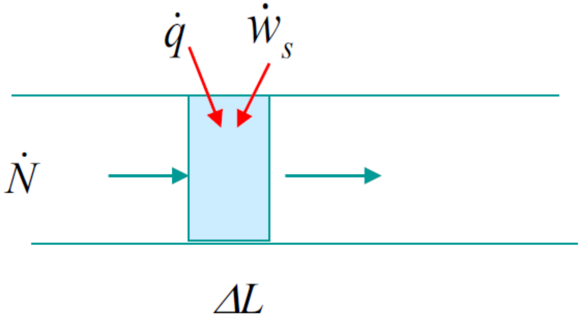
- **For an isothermal flow engine ($T_1 = T_2 = T$)** → $\dot{W}_s=-\dot{N}_1\left(\underline{G}_1-\underline{G}_2\right)+T\dot{S}_{gen}$
- **For an isothermal, reversible process** → $\left(\dot{W}_s\right)^{rev}=-\dot{N}_1\left(\underline{G}_1-\underline{G}_2\right)$
- **For an adiabatic process** → $\left(\dot{W}_s\right)^{adiabatic}=-\dot{N}_1\left(\underline{H}_1-\underline{H}_2\right)$

$$0=\dot{N}_1\left(\underline{S}_1-\underline{S}_2\right)+\dot{S}_{gen}$$

- **For an adiabatic and reversible process (isentropic process)** → $0=\dot{N}_1\left(\underline{S}_1-\underline{S}_2\right)\ \Rightarrow \boxed{\underline{S}_1=\underline{S}_2}$

Continuous flow systems

- **Compressor and turbines**
- **Shell balance at steady state,**



$$\frac{d\dot{N}}{dL} = 0$$

$$\dot{N}\frac{d\underline{H}}{dL} = \dot{q} + \dot{w}_s$$

$$\dot{N}\frac{d\underline{S}}{dL} = \frac{\dot{q}}{T} + \dot{\sigma}_{gen}$$

For a reversible process,

$$\dot{\sigma}_{gen} = 0$$

$$\dot{q}^{rev} = \dot{N}T\frac{d\underline{S}}{dL} \Rightarrow \dot{w}_s^{rev} = \dot{N}\frac{d\underline{H}}{dL} - \dot{N}T\frac{d\underline{S}}{dL}$$

$$\frac{\dot{w}_s^{rev}}{\dot{N}}dL = d\underline{H} - T\,d\underline{S} = d\underline{U} + P\,d\underline{V} + \underline{V}\,dP - Td\underline{S} = \underline{V}\,dP$$

$$\underline{W}_s^{rev} = \int \frac{\dot{w}_s^{rev}}{\dot{N}}dL = \int \underline{V}\,dP$$

Continuous flow systems

- ***For the ideal gas undergoing an isothermal change.*** $P\underline{V} = RT$,

$$\underline{W}_s = \int \underline{V}\, dP = \int \frac{RT}{P} dP = RT \int \frac{dP}{P} = RT\ ln \frac{P_2}{P_1}$$

- **An expansion or compression follows a polytropic process,** $P_1\underline{V}_1^{\gamma} = P_2\underline{V}_2^{\gamma}$ **= constant,**

$$\underline{W}_s = (constant)^{1/\gamma} \int \frac{dP}{P^{1/\gamma}} = \frac{\gamma\left(P_2\underline{V}_2 - P_1\underline{V}_1\right)}{\gamma - 1}$$

For an ideal gas

$$\gamma = 0 \Rightarrow \text{for an isobaric process}$$

$$\gamma = 1 \Rightarrow \text{for an isothermal process}$$

$$\gamma = \infty \Rightarrow \text{for a constant volume (isochoric) process } \left[\underline{W}_s = \underline{V}\left(P_2 - P_1\right)\right]$$

$$\gamma = C_P^*/C_V^* \Rightarrow \text{for a constant entropy (isentropic) process (ideal gas \& constant } C_P\text{)}$$

- **In calculating the changes of state variables (such as *U*, *S*, *A*, *G*, ---), any convenient path can be used (frequently, reversible path)**

Heat, Works, and Engines

- A polytropic process:
  - Fluid during an expansion (or compression):

$$P\underline{V}_1^{\gamma} = P\underline{V}_2^{\gamma} = \text{constant}$$

For an ideal gas,

  - γ = 0 for an isobaric process.
  - γ = 1 for an isothermal process.
  - $\gamma = \infty$ for an isochoric (constant-V) process.
  - $\gamma = C_P^* / C_V^*$

?

- Work from a reversible flow-type engine following polytropic process,

$$\dot{\underline{W}}_S^{rev} = \int \underline{V} dP = c^{1/\gamma} \int \frac{dP}{P^{1/\gamma}} = \dots = \frac{\gamma(P_2\underline{V}_2 - P_1\underline{V}_1)}{\gamma - 1}$$

4.4 Entropy changes of matter

- **For an ideal gas**

$$d\underline{U} = C_V^* dT\ ,\quad P = RT/\underline{V}\ ,\quad C_P^* = C_V^* + R$$

$$d\underline{S} = \frac{1}{T}d\underline{U} + \frac{P}{T}d\underline{V} = \frac{C_V^*}{T}dT + \frac{R}{\underline{V}}d\underline{V}$$

$$\underline{S}(T_2,\ \underline{V}_2) - \underline{S}(T_1,\ \underline{V}_1) = C_V^*\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{\underline{V}_2}{\underline{V}_1}\right)$$

$$\underline{S}(T_2,\ P_2) - \underline{S}(T_1,\ P_1) = C_P^*\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$$

$$\underline{S}(P_2,\ \underline{V}_2) - \underline{S}(P_1,\ \underline{V}_1) = C_P^*\ln\left(\frac{\underline{V}_2}{\underline{V}_1}\right) + C_V^*\ln\left(\frac{P_2}{P_1}\right)$$

- **For a solid or liquid**

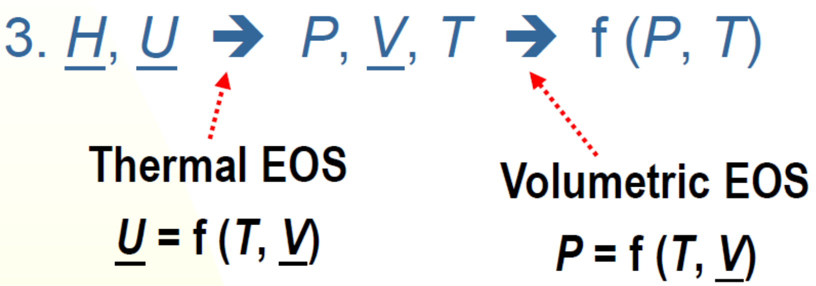
$$d\underline{S} = \frac{1}{T}d\underline{U} + \frac{P}{T}d\underline{V} \approx \frac{1}{T}d\underline{U}$$

$$\text{also } C_V \approx C_P \text{ for liquids \& solids,}$$

$$d\underline{U} = C_V dT \approx C_P dT \Rightarrow d\underline{S} \approx C_P\frac{dT}{T} \Rightarrow \underline{S}(T_2) - \underline{S}(T_1) \approx \int_{T_1}^{T_2} C_P\frac{dT}{T}$$

4.5 Applications of entropy balance

- 1. system choice
- 2. mass and energy balance equations
- 3. $\underline{H}, \underline{U} \rightarrow P, \underline{V}, T \rightarrow f(P, T)$



Thermal EOS

$\underline{U} = f(T, \underline{V})$

Volumetric EOS

$P = f(T, \underline{V})$

- 4. balance eqs. → $f(P, T, \text{mass}, W_s, Q)$
- 5. If number of unknown = number of the equations →

  <<The problem can be solved>>

  If number of unknown > number of the equations →

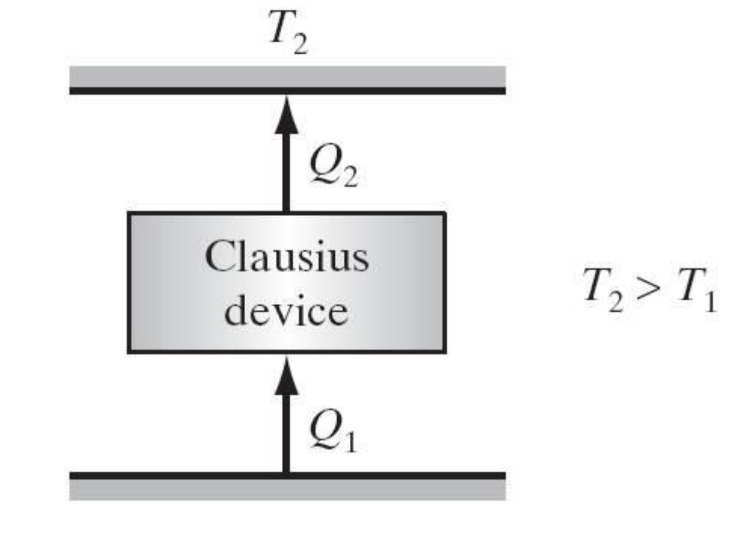
  <<Need additional balance equations>>

  e.g., entropy balance equations

Entropy: A New Concept

- Ex.4.1-1

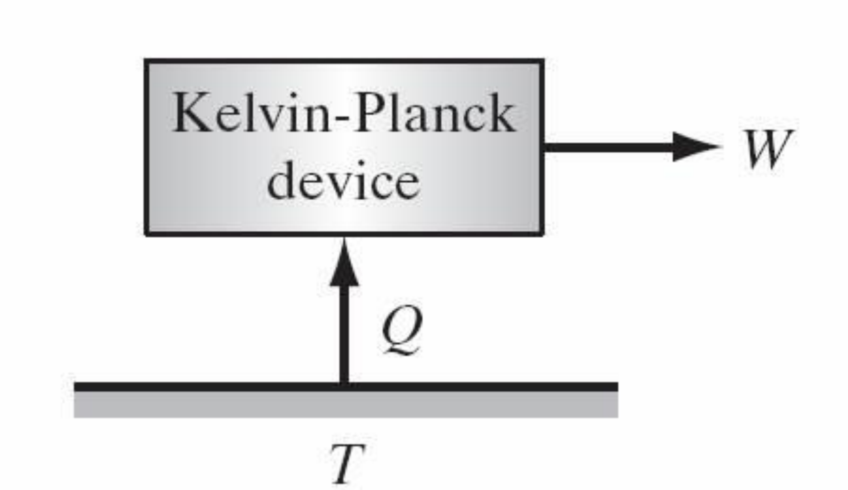
  The 2nd law statement of R. Clausius (1822-1888) is that it is not possible to transfer heat from a colder body to a hotter body. Show form the axiom $S_{gen} \geq 0$ that the process below is impossible.



Entropy: A New Concept

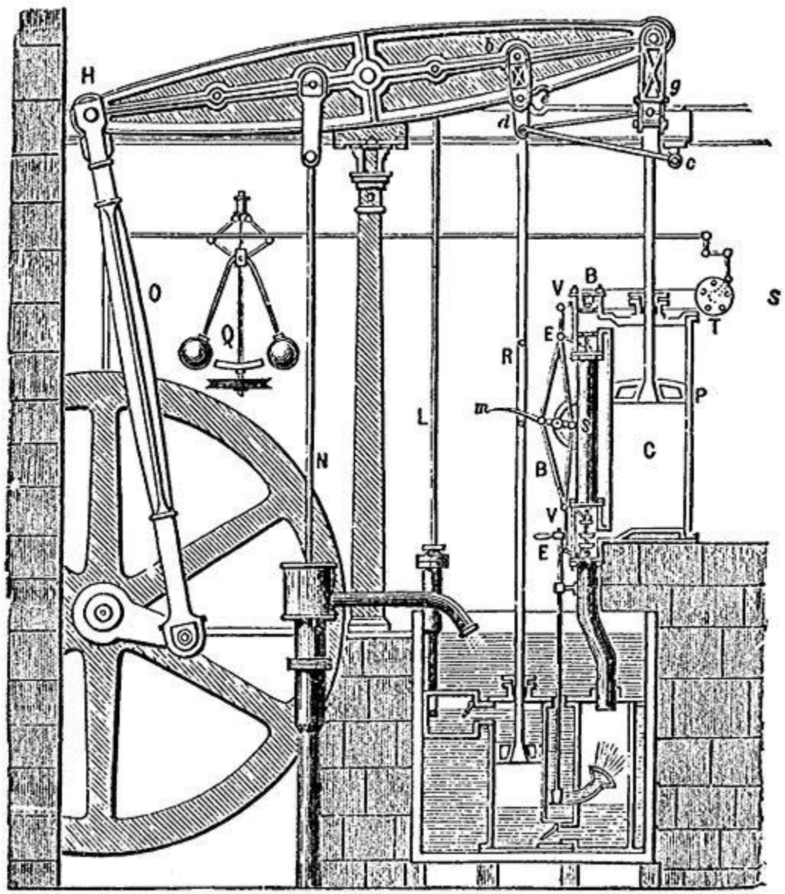
- Ex.4.1-2

  An alternative statement of the 2nd law, due to Lord Kelvin (William Thomson,1824-1907) and Max Planck (1858-1947), is that it is not possible to construct a device operating in a cycle that results in non effect other than the production of work by transferring heat from a single body. Show form the axiom $S_{gen} \geq 0$ that the process below is impossible.



Entropy: A New Concept

- From Heat to Work, e.g., Steam Engine



Boulton & Watt 1784 (from wikipedia)

HW:

- Find out how this steam engine works.
- What is the implication of that “heat cannot be completely converted to work”

NOTE:

1. We can use other medium instead of H_2O.
2. If the heat comes from a combustion reaction, it is called the combustion engine.

Examples

Solar Energy Conversion

- Ex.4.3-1

  Show that a solar or photovoltaic cell that converts solar energy to mechanical energy or electrical energy must emit some of the energy of the incident radiation as heat.

Solar Energy Conversion

- Ex.4.3-2

  Based on analysis distribution of the frequency distribution from the sun, it can be considered to be emitting radiant energy with a Stefan-Boltzmann distribution at 6000 K. Estimate the maximum efficiency with which this radiant energy can be converted to electrical energy using solar cells. For this analysis, assume that the solar cell is operating in steady state and is receiving radiant energy, that its surface temperature is 300 K, and that it is losing heat by conduction to the environment.

Entropy Changes of Matter

- For a closed system:
  - Mass balance: $\Delta M = M_{t2} - M_{t1} = 0$
  - Energy balance: $\Delta U = U_f - U_i = Q + W$
  - Entropy balance: $\Delta S = S_f - S_i = \frac{Q}{T} + S_{gen}$
- Both U and S are state properties. Therefore,
  - change of U with respect to the state of a system can be analyzed by the above energy balance equation.
  - change of S with respect to the state of a system can be analyzed by the above energy balance equation when assuming reversible process.

Entropy Changes of Matter

- It was also shown earlier that for a closed system

$$dU = TdS - PdV \quad \text{or} \quad d\underline{U} = Td\underline{S} - Pd\underline{V}$$

i.e.,

$$d\underline{S} = \frac{d\underline{U}}{T} + \frac{Pd\underline{V}}{T}$$

NOTE the concept of “state property”.

- For an ideal gas (in a closed system):
  - $d\underline{U} = C_V^* dT \quad \text{and} \quad P = RT/\underline{V}$

$$\therefore d\underline{S} = \frac{d\underline{U}}{T} + \frac{Pd\underline{V}}{T} = \frac{C_V^* dT}{T} + \frac{Rd\underline{V}}{\underline{V}}$$

$$\underline{S}(T_2,\underline{V}_2) - \underline{S}(T_1,\underline{V}_1) = C_V^* \ln(\frac{T_2}{T_1}) + R\ln(\frac{\underline{V}_2}{\underline{V}_1})$$

  - Using the ideal gas law, this eqn can be transformed to

$$\underline{S}(T_2,P_2) - \underline{S}(T_1,P_1) = C_P^* \ln(\frac{T_2}{T_1}) - R\ln(\frac{P_2}{P_1})$$

$$\underline{S}(P_2,\underline{V}_2) - \underline{S}(P_1,\underline{V}_1) = C_V^* \ln(\frac{P_2}{P_1}) + C_P^* \ln(\frac{\underline{V}_2}{\underline{V}_1})$$

Entropy Changes of Matter

- For liquids and solids:
  - $d\underline{U} = C_V dT \approx C_P \mathrm{dT}$ and $d\underline{V} <<$

$$\therefore d\underline{S} = \frac{d\underline{U}}{T} + \frac{Pd\underline{V}}{T} \approx \frac{C_P dT}{T}$$

$$\underline{S}(T_2) - \underline{S}(T_1) = \int_{T_1}^{T_2} C_P \frac{dT}{T}$$

NOTE the concept of “state property”.

- S with respect to the state of matters can be available from Tables (e.g., steam table) and charts (e.g., T-S diagram or P-H shown in Ch.3).

Entropy Changes of Matter

- Ex.4.4-1

  Compute the entropy change on mixing 1 kg of steam at 1 bar and 200 ^{o}C with 1 kg of steam at 1 bar and 300 ^{o}C. of water.

- Ex.4.4-2

  Compute the entropy generated by the flow of 1 kg/s of steam at 400 bar and 500 ^{o}C undergoing a Joule-Thompson expansion to 1 bar.

Entropy Balance Equation

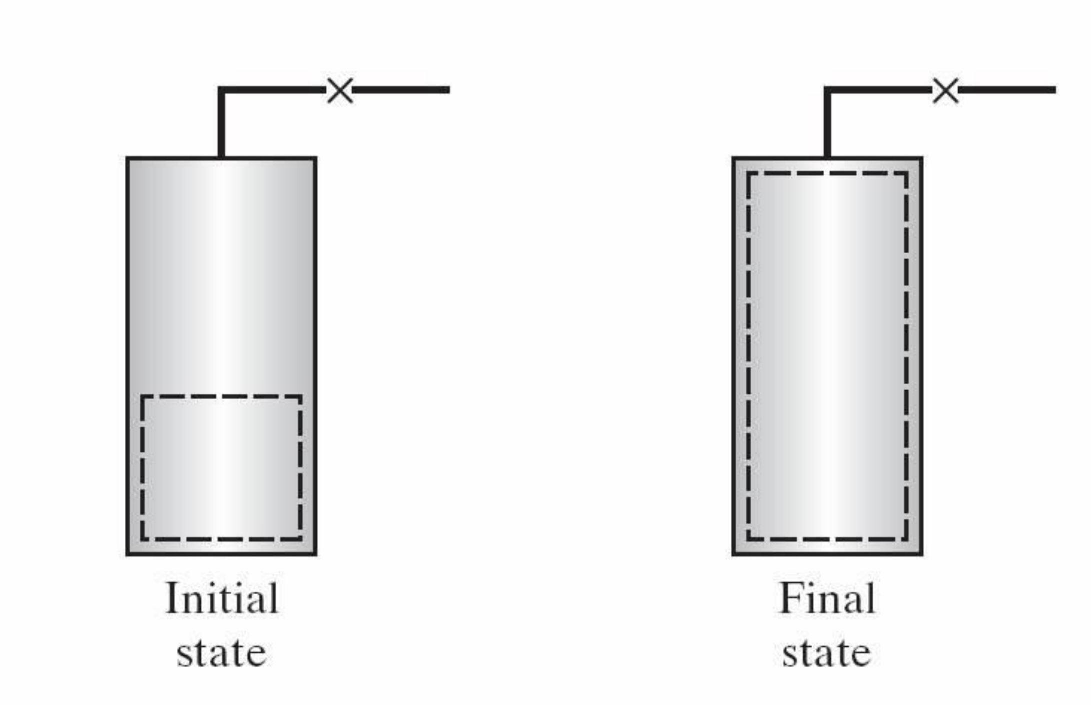
- Ex.4.5-1

  Estimate the exit temperature and power requirement for a gas compressor and include the entropy balance analysis. As in Ex.3.4-4, assuming that the inlet to the compressor is air (as an ideal gas with C_P =29.3 J/mol K) at 1 bar and 290 K and that the discharge is at 10 bar, estimate the temperature of the exit gas and the rate at which work is done on the gas for a gas flow of 2.5 mol/s. .

Entropy Balance Equation

- Ex.4.5-2

  For the case of a compressed gas cylinder connected to another evacuated cylinder (Ex.3.4-5), consider the following choice of system and apply the entropy balance.



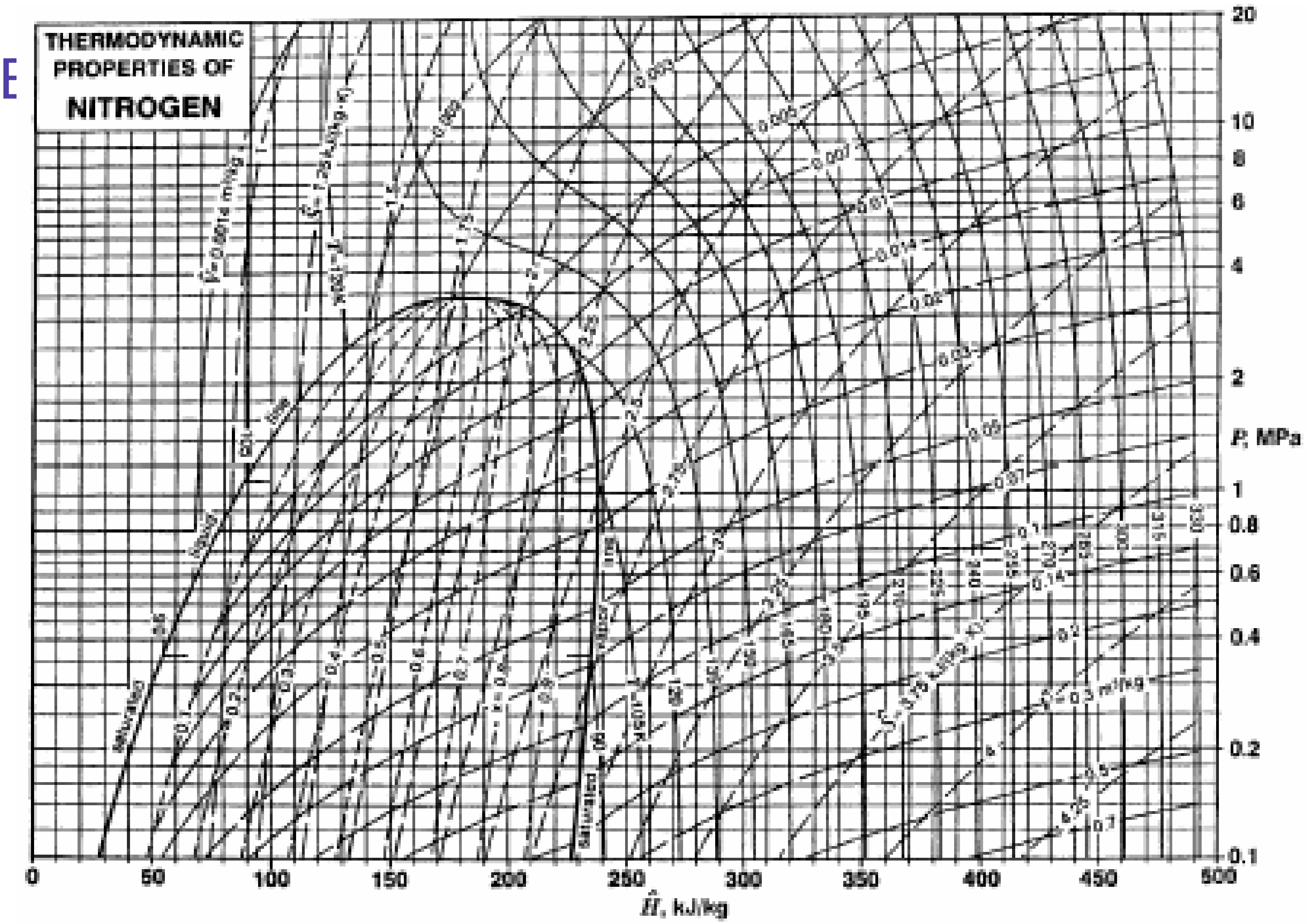
Entropy Balance Equation

- Ex.4.5-3

  (Ex.3.4-5 continued) A gas cylinder of 1 m^3 containing N_2 at 40 bar and 200 K is connected to another cylinder of 1 m^3, which is evacuated. A valve between the two cylinders is opened until the pressure in the cylinders equalize and then is closed. Find the final temperature and pressure in each cylinder if no heat flows into or out of the cylinders or between the gas and the cylinder. walls. The gas is ideal with a constant-pressure heat capacity of 29.3 J/mol K.

Entropy Balance Equation

- E

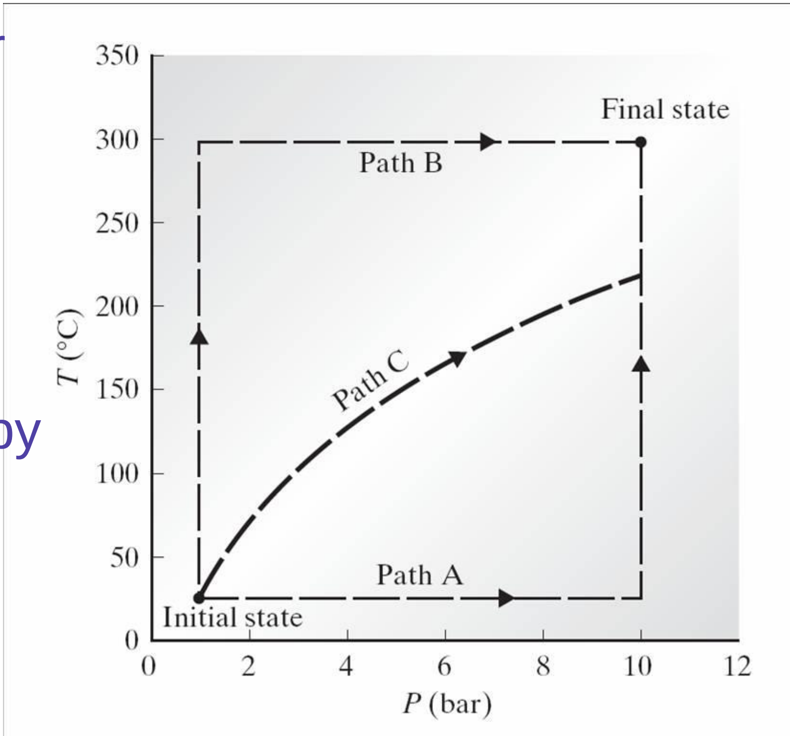


Entropy Balance Equation

- Ex.4.5-4

(Ex.3.4-6 continued) Show that the entropy S is a state function by computing ΔS for each of the three paths.

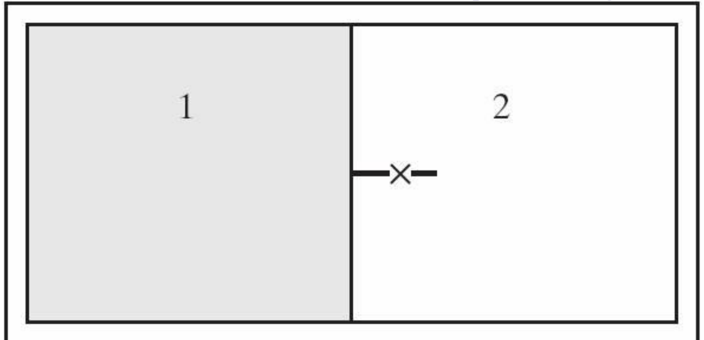
(a) Isothermal compression to 10 bar and then isobaric heating to 300 °C.
(b) Isobaric heating to 300 °C following by isothermal compression to 10 bar.
(c) A compression in which PV^{γ} = constant, where $\gamma = C_P/C_V$, followed by an isobaric cooling or heating, if necessary, to 300 °C.



Entropy Balance Equation

- Ex.4.5-5 (max S at equilibrium)

  A well-insulated box of volume 6 m^3 is divided into two equal volumes. The left-hand cell is initially filled with air at 100 ^{o}C and 2 bar, and the right-hand cell is initially evacuated. The valve connecting the two cells will be open so that gas will slowly pass from cell 1 to cell 2. The wall connecting the two cells conducts heat sufficiently well that the temperature of the two cells will always be the same. Plot the pressure change of both cells and (2) the change of total entropy. Air can be considered as an ideal gas of constant heat capacity in this case.

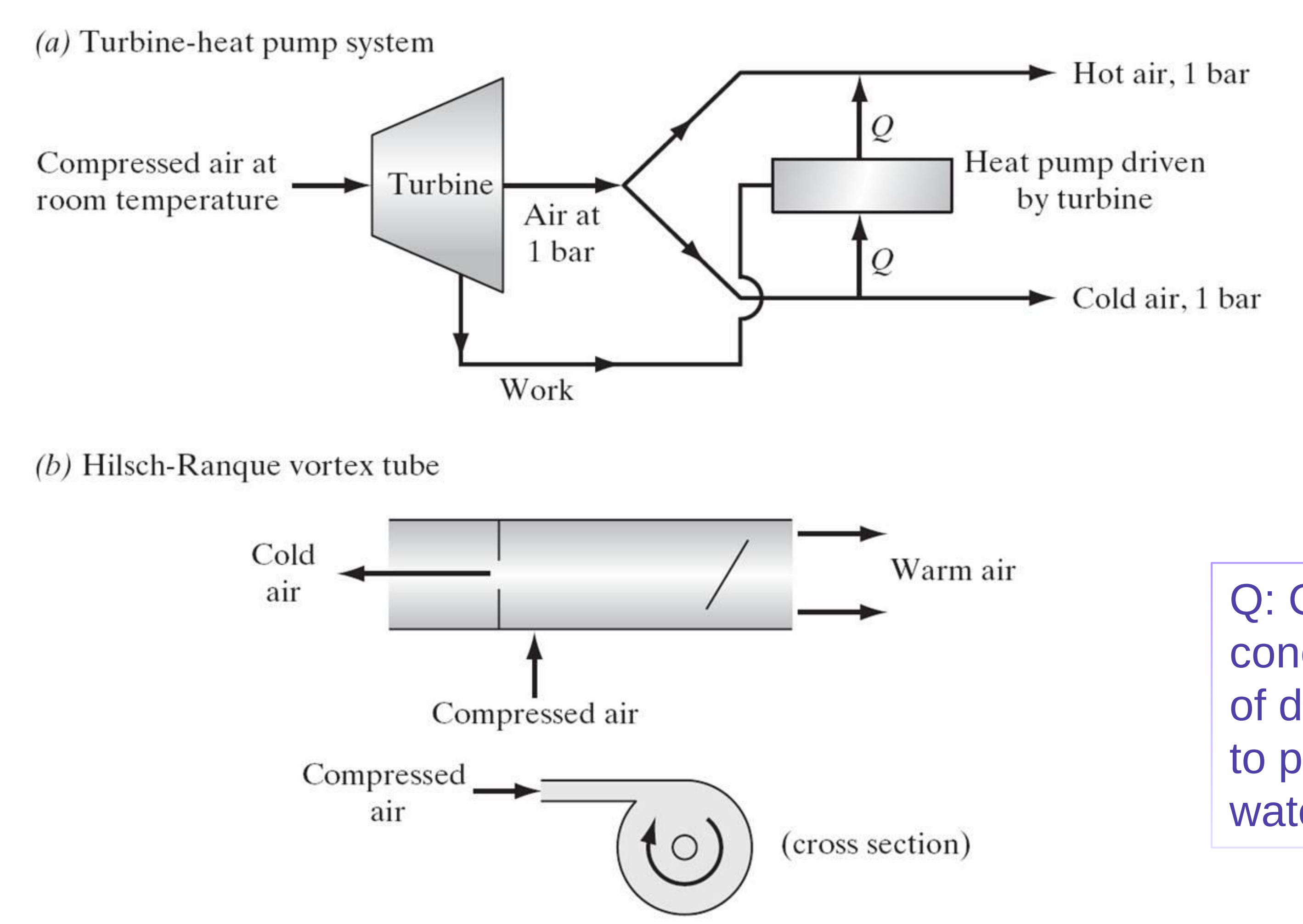


Entropy Balance Equation

- Ex.4.5-6

  An engineer claims to have invented a steady-flow device that will take air at 4 bar and 20 ^{o}C and separate it into two streams of equal mass, one at 1 bar and -20 ^{o}C and the second at 1 bar and 60 ^{o}C. Furthermore, the inventor states that his device operates adiabatically and does not require (or produce) work. Is such a device possible? Air can be considered as an ideal gas of constant heat capacity of $C_P^* = 29.3$ J/(mol K).

Entropy Balance Equation



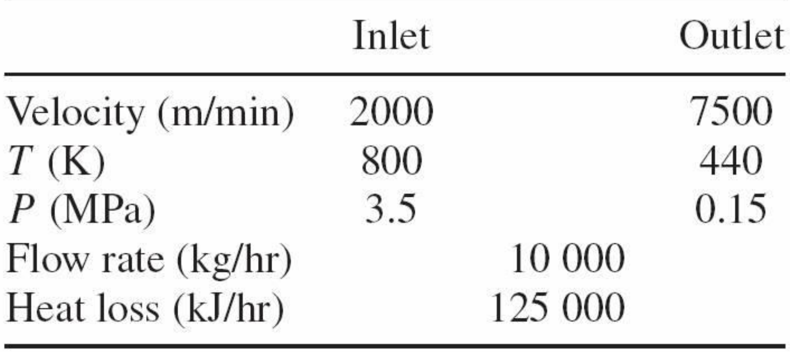
Q: Can you apply this concept in the design of drinking water stand to provide both chilled water and hot water?

f4_5_5

Entropy Balance Equation

- Ex.4.5-7

A steam turbine operates at the following conditions:



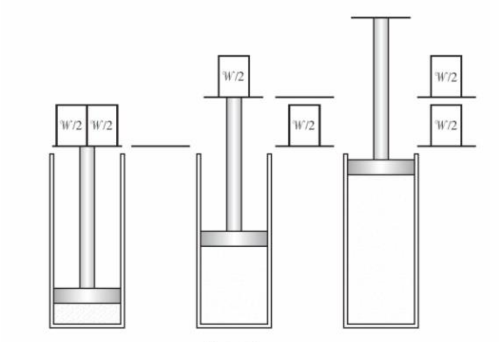
	Inlet	Outlet
Velocity (m/min)	2000	7500
T (K)	800	440
P (MPa)	3.5	0.15
Flow rate (kg/hr)	10 000	
Heat loss (kJ/hr)	125 000	

a. Compute the horsepower developed by the turbine and the entropy change of the steam.

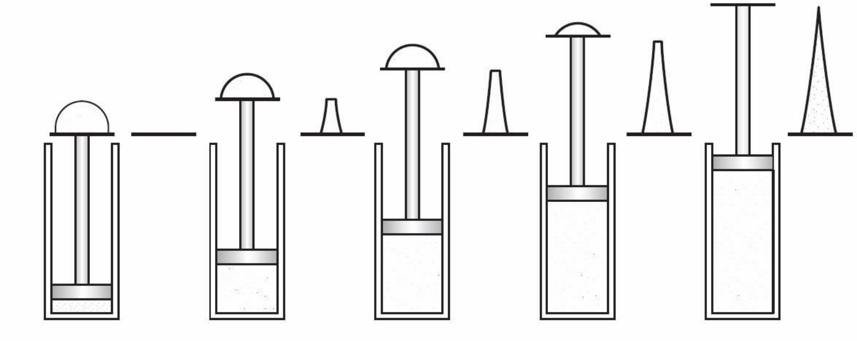
b. Suppose the turbine is replaced with one that is well insulated, so that the heat loss is eliminated, and well designed, so that expansion is reversible. If the exit pressure and velocity are maintained at the previous values, what are the outlet steam temperature and the horsepower developed by the turbine?

Entropy Balance Equation

- Ex.4.5-8 (S_{gen} = o for reversible processes)
  - a. By considering only the gas contained within the piston-and-cylinder device of Ex 3.4-7 to be the system, show that the gas undergoes a reversible expansion in each of the four processes.
  - b. By considering the gas, piston, and cylinder to be the system, show that the processes a, b, and c are not reversible and that process d is reversible.



Process b



Process d

Entropy and Exergy

- P.4.31 (useful work, availability, exergy)
  - a. Useful work of a process = (the total work done by the system) – (the work done in expansion of the system boundaries).
  - b. The maximum useful work is obtained with reversible process and all heat transfer to surrounding T_o. Also, the feed and exit streams in an open system should be at ambient conditions.
  - c. For a close system, $W_u^{max} = A_2 - A_1$, where $A = U + P_oV - T_0S$

    e.g., 1 kg steam in a piston-and-cylinder system change from 30 bar, 600 ^oC to 5 bar, 300 ^oC,

    $$\boxed{\eta = \frac{W_u}{W_u^{max}}}$$
  - d. For an open system at steady state, $W_u^{max} = M(\hat{B}_2 - \hat{B}_1)$, where $\hat{B} = \hat{H} - T_0\hat{S}$

    e.g., a coal-fired power plant generates ca. 2.2 kWh for each kg of coal burned,

    $$\boxed{\eta = \frac{W_u}{W_u^{max}}}$$